

ROLE OF CHAR DURING REBURNING OF NITROGEN OXIDES

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ABSTRACT

The progress in this quarter includes four parts. In the first segment, the implications of our data reported in the last quarter are discussed further. BET N_2 surface area does not seem to be the only contributing factor to the remarkable activity of lignite char during reburning, and chars of different origins probably have different controlling steps in the overall surface reaction mechanisms. Unlike NO reduction in the gas phase, oxygen inhibits the heterogeneous mechanisms.

The second part of this report justifies the use of our laminar flow reactor system for the measurement of reaction rate. Dispersion model is used in the analysis.

An expression relating the rate constant with the experimentally obtainable NO conversion for our flow reactor have been derived. Rates of NO/char reaction for six series of experiments have been measured over the temperature range 800 to 1100 °C. These six series of experiments have been conducted with two different chars, one bituminous coal char and one lignite char, and three different levels of feed NO concentrations, 200, 400 and 1000 ppm. Results from the comparison of char activities suggest that, **in the absence of O_2 and CO_2 , the origin of char is not a significant factor for NO reduction.** The CO/ CO_2 ratio in the products is higher than one under all test conditions, but the ratio increases with increasing feed NO concentrations. Recoveries of oxygen from the lignite char at temperatures above 1050 °C is higher than 1 indicating gasification of organic oxygen in the char.

Surface areas of selected chars after devolatilization and after reburning have been analyzed by BET in N_2 . Results indicated char surface area changes after reburning, which is caused either by the higher temperature of reburning or by surface reaction.

I. INTRODUCTION

The regulations established by the Clean Air Act Amendments of 1990 in the United States mean that a single NO_x control technology is not likely to be sufficient for boilers in the ozone non-attainment areas. Reburning is an emerging three-stage combustion technology designed for the reduction of NO by introducing a small amount of reburning fuel above the primary flame where the majority of NO is chemically reduced to nitrogen in this fuel rich environment. The concept of reburning was first introduced by Wendt *et al.* (1973). Tests on a full-scale boiler at Mitsubishi Heavy Industries (Takahashi *et al.*, 1983) resulted in over 50% NO_x reduction.

Coals, including lignites, are an economical source of carbon required for NO reduction in the fuel rich environment. Its effectiveness as a reburning fuel depends on two seemingly unfavorable factors. First, a fraction of the nitrogen in coal will be converted to NO in the reburning and burnout stages. Conversion of volatile nitrogen during reburning has been the objective of an earlier study of ours (Burch *et al.*, 1994). Second, while the homogeneous gas phase NO reduction in the fuel rich environment is relatively well understood (e.g., Miller and Bowman, 1989), the NO reburning by chars of diverse origin and history has not been the major objective of a systematic investigation.

Our previous studies of simulated reburning with reactors of two scales (Burch *et al.*, 1991a,b; 1994; Chen *et al.*, 1991) have demonstrated that lignites are more effective than methane. The two lignites tested were selected from Mississippi and North Dakota; both lignites have high contents of calcium. Initial screening with the North Dakota lignite indicated that the lignite char surface participates in heterogeneous/catalytic NO reduction to HCN, while lignite ash enhances catalytic HCN reduction to NH₃. Both reactions are important in the overall NO reduction scheme. The effectiveness of lignite for NO reduction during reburning has recently been demonstrated in a

1.0 MMBtu/hr pilot scale test facility (Payne *et al.*, 1995).

Detailed kinetic analysis of homogeneous phase NO reduction in fuel rich environment indicates that the majority of NO is reduced by hydrocarbon radicals C, CH and CH₂ to HCN and amine radicals (NH₂) (Miller and Bowman, 1989). The amine radicals, in turn, can be converted to N₂ or NO. The yields of these desirable hydrocarbons radicals from lignite during reburning are not known. Nevertheless, coal and lignite produce only about 50% of the volatile carbons of that which methane produces at the same stoichiometry, which led to the speculation that the lignite char participates in considerable heterogeneous reactions with NO.

Although NO reburning by char has not been a major area of research, investigating the interactions of NO and carbonaceous materials has been the objective of a number of studies. An extensive review has been conducted by De Soete (1990). It has been shown that carbonaceous materials can be gasified by NO to form CO, CO₂ and N₂ (Bedjai *et al.*, 1958; Smith *et al.*, 1959; Furusawa *et al.*, 1980; Levy *et al.*, 1981; Chan *et al.*, 1983; Suuberg *et al.*, 1990; Teng *et al.*, 1992; Chu and Schmidt, 1993; Illan-Gomez *et al.*, 1993). The gasification reaction can be promoted by the addition of reducing agents, such as CO and H₂, and inhibited by O₂ when the CO₂/CO ratio is higher than one (De Soete, 1990). In addition to gasification, reaction of NO with CO on various surfaces, including char, ash and soot, can also be a major route of heterogeneous NO reduction mechanisms (De Soete, 1990). Catalytic decomposition of NO on various metallic oxides, some are common constituents in the lignite, has been reported by Winter (1971).

Huffman *et al.* (1990) reported that calcium is dispersed in coal macerals and is bonded to the oxygen anions. During combustion, the calcium present in lignite agglomerates, and eventually forms CaO and CaS. Recent lab-scale investigations of fluidized bed combustion (FBC) and circulating

FBC (CFBC) have shown that calcium sulfide (Hansen *et al.*, 1992), CaO (Allen, 1991; Hansen *et al.*, 1992; Hansen and Dam-Johansen, 1993; Shimizu *et al.*, 1993; Lin *et al.*, 1993) and Fe₂O₃ (Allen, 1991) serve as catalysts for NO reduction in various environments. While most of these researchers claimed that these catalysts enhanced the gasification or the conversion of NO + CO to form CO₂ and N₂, Lin *et al.* indicated that CO decreases the NH₃ conversion to NO. Lin *et al.* also claimed that NO may oxidize NH₃ to form nitrogen through homogeneous and heterogeneous mechanisms in FBC or CFBC. These char gasification and mineral-catalyzed reactions in reburning environment have not been fully investigated, but can certainly be enhanced by the highly porous nature of lignite char. The complexity of calcium-NO interactions has been demonstrated by infrared studies (Low and Yang, 1974; Allen, 1990).

The effects of calcium during oxidation of various solid carbonaceous materials has also been examined through a class of impregnation/ion-exchange techniques (Walker *et al.*, 1979; Radovic *et al.*, 1983; Hengel and Walker, 1984; Radovic *et al.*, 1985; and Levendis *et al.*, 1989). In a study of the catalytic effects of ion-exchange of lignite on char oxidation, Walker *et al.* found that the reactivity of various calcium-containing chars in air, CO₂ and water vapor increased linearly with increasing calcium. Radovic *et al.* discovered that the well-dispersed calcium oxide formed upon pyrolysis of lignites is a very efficient *in situ* catalyst for sulfur capture. The char reactivity decreases with the increasing severity of pyrolysis conditions which is probably due to CaO crystallite growth. Levendis *et al.* reported that carbon oxidation can be catalyzed by calcium up to 2 orders of magnitude.

Mild oxidation has been used to enhance the oxygen functional groups and the subsequent ion-exchange capability of carbonaceous materials (Chang *et al.*, 1986). Following the same concept,

Bartholomew *et al.* (1991) and Gopalakrishnan *et al.* (1994) produced char in the presence of oxygen and used the same ion-exchange/impregnation procedure discussed above. Their results indicate significant catalytic effects: up to a 160-fold increase for CaCO_3 catalysis, a 290-fold increase for CaSO_4 , and up to 2700 times for CaO .

While most of the studies in the literature have been centered around the Ca-catalyzed char oxidation by oxygen, Wojtowicz *et al.* (1991) reported that oxidation of a peat char by N_2O during fluidized bed combustion can be catalyzed by impregnating the char with CaO . Recently, Illan-Gomez *et al.* (1995) reported that calcium catalyzes NO-carbon reaction at 300 to 600°C through a mechanism that is consistent with the formation of intermediate CaO(O) surface species.

The primary objectives of this study are to investigate the extend and to improve the understanding of heterogeneous NO reduction mechanisms during reburning with coal and lignite. The extend of heterogeneous mechanisms of NO reduction on lignite char has been demonstrated and documented in the last quarter (Chen *et al.*, 1995). During this quarter, we examine the effect of surface area, and results seems to indicate chars from different origins are governed by different mechanisms or different surface reaction steps. The use of our laminar flow reactor system is theoretically justified by a dispersion model. The rates of NO reaction with chars derived from a bituminous coal and a lignite have been measured with inlet NO concentration at 200, 400, and 1000 ppm., and in the temperature range 800 to 1100 °C.

II. WORK ACCOMPLISHED

The detailed flow reactor system for reburning and experimental procedure have been discussed by Burch *et al.* (1991a,b). The detailed char preparation procedure has been documented

in our sixth quarterly report (Chen *et al.*, 1995).

A. Implications of Surface Reaction Mechanisms

Resorting to a first level analysis discussed below, the data presented in Figures 1 and 2 seem to imply that detailed analysis of surface reactions are important for NO reburning with lignite char. Our earlier calculations indicated that internal and external mass transfers should not be the limiting steps in a system involving lignite char (Chen *et al.*, 1994); thus, kinetic analysis should be focused on adsorption, desorption, and surface reaction mechanisms. For the NO reaction with char, a dual-site dissociative adsorption model (Beer *et al.*, 1980; De Soete, 1990) results in the following Langmuir rate expression linearly proportional to surface area (i.e., total active sites), and to NO concentration when NO concentration is low.

$$-\frac{d(NO)}{dt} = \frac{k K_{NO} P_{NO}}{1 + K_{NO} P_{NO}} \quad (A-1)$$

where P_{NO} is the partial NO pressure in the gas phase, k the rate constant, and K_{NO} the adsorption constant of NO on the solid. From our BET analysis in nitrogen, surface areas of chars after pyrolysis are 20.1 and 66.9 m²/g for chars derived from bituminous coal and Mississippi lignite, respectively. Surface areas of chars after reburning at SR=0.9 decrease to 11.9 and 44.1 m²/g for chars derived from bituminous coal and Mississippi lignite, respectively. Assuming the NO reduction follows first order rate expression with Arrhenius constant k , a four-fold increase in surface area causes cubic increase in NO conversion after reaction time t .

$$\frac{1 - (\text{conversion on lignite char}, x_2)}{1 - (\text{conversion on bituminous coal char}, x_1)} = \frac{e^{-4kt}}{e^{-kt}} = e^{-3kt} = (1 - x_1)^3 \quad (\text{A-2})$$

Data in Figures 6 and 8 indicate the ratio of exit NO concentrations during reburning with chars derived from the two different origins is higher than the cubic relation in Eq. (A-2). For instance, NO conversion by char derived from bituminous coal at SR=0.75 is 0.08 (Figure 2), and the NO yield caused by a four-fold increase in surface area should be $(1-0.08)^3 = 0.78$. Nevertheless, the NO yield from reburning with char derived from lignite at SR=0.75 is only 0.18. This analysis suggests that surface area alone is not able to contribute to the high conversion observed from reburning with lignite char, and chars of different origins seem to follow different mechanisms or to have different controlling steps in the overall reaction scheme.

The observed decrease in surface areas of chars during reburning may be due to a structure ordering of carbon, or graphitization, taking place at elevated temperatures (Sahu *et al.*, 1988; Wong *et al.*, 1995). The structure reorganization of the carbon matrix at higher pyrolysis temperature, up to 1300 °C, leads to closure of pore mouths and pore coalescence, thus reducing surface area. Reburning of this study was conducted at 1100 °C, a temperature higher than the pyrolysis temperature, 950 °C.

It is interesting to note that, for most reburning fuels, the exit NO emissions monotonically decrease with the increasing quantity of fuels (Chen *et al.*, 1995). Methane is the only exception among the fuels studied, which has a minimum yield at SR=0.9. In an earlier study of ours (Burch *et al.*, 1991b), the optimum SR were also observed for two other volatile fuels, hexane and benzene. The difference in NO yields from reburning with volatile and lignites seems to distinguish the

heterogeneous mechanisms from the homogeneous mechanisms. Myerson (1974) has postulated that gas phase NO reduction requires oxygen radicals to initiate the chain reaction; therefore, NO reburning efficiency decreases when excessive volatile fuel is added. Figure 1 and 2 indicate that oxygen is not required when lignites and chars are used during reburning. The Langmuir-Hinshelwood models of NO reduction on the activated carbon in the literature (Smith *et al.*, 1959; Sheppard, 1974; Beer *et al.*, 1980; De Soete, 1990) have suggested that adsorption of NO is a rate limiting step and surface oxygen complex inhibits NO reduction. The results in Figure 2 are consistent with these models, and seem to indicate the importance of heterogeneous mechanisms during reburning with lignite.

B. Characteristics of Flow Reactor System

The Reynolds number of the gas in the flow reactor decreases from 2 to 1 in the temperature range 800 to 1100 °C. Concern arises if such low Reynolds number contributes errors to the measurement of reaction rate or to the nonideal solid mixing. The objective of the following analysis is to resolve these questions.

1. Effects of Laminar Flow and Dispersions on Rate Measurements

It is known that measurement of reaction rate can be profoundly influenced by the flow pattern inside a laminar flow reactor. For estimation of the extends of such effects, the flow region based on the Peclet number is estimated first, and the choice of axial dispersion model is justified. Based on the dispersion model, the extends of radial and axial diffusions are estimated and the deviations from a plug-flow in the estimation of rate constant are assessed. In the second part of the section, char dispersion and velocity in the reactor are discussed.

Although the reaction in a tubular flow reactor can be affected by a number of variables, the flow pattern has been conveniently categorized into three regions (e.g., Wen and Fan, 1975): pure convection, axial dispersion, and intermediate region that has to rely on numerical solution. The two factors governing the flow regions are: Peclet number (Ru/D_M) and dimensionless time ($D_M t/R^2$), where R is the tube radius, u is the average fluid velocity, D_M is the molecular diffusivity, and t is the average fluid residence time in the reactor. Our experiments have been conducted with a tubular reactor with i.d. 1.91 cm, at 1100 °C, and with a volumetric flow rate 2000 cm³/min (measured at 25 °C). The reactor is placed in a electric furnace with a 12 in heating element. Using property data for the simulated flue gas composition and method of Sellars *et al.* (1956), the maximum gas temperature is estimated to be 50 °C lower than the maximum wall temperature and to be maintained for only 4 in of the tube length. The estimated average gas temperature and reaction time for this 4 in zone are the basis for the analysis presented below. At 1100 °C, the flow rate and average residence time of gas in the tube are 153.6 cm³/s and 0.2 s, respectively. The diffusivity of NO in He can be estimated based on molecular theory (Bird *et al.*, 1960)

$$\frac{P D_{AB}}{(P_{cA} P_{cB})^{\frac{1}{3}} (T_{cA} T_{cB})^{\frac{5}{12}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}} = a \left(\frac{T}{\sqrt{T_{cA} T_{cB}}} \right)^b \quad (\text{B-1})$$

in which D_{AB} [=] cm² sec⁻¹, p [=] atm, and T [=] °K. Analysis of experimental data gave the following values of the constants a and b : $a = 2.745 \times 10^{-4}$ and $b = 1.823$ (Bird *et al.*, 1960). This formula suggests that the diffusivity varies from 0.84 to 13.7 cm²/s when temperature increases from 25 to 1100 °C. Based on the system parameters obtained above, the Peclet number and dimensionless

reaction time at 1100 °C are estimated

$$Ru/D_M = 3.72 \quad (B-2)$$

$$D_M t/R^2 = 2.99 \quad (B-3)$$

The values of these two factors imply that the axial dispersion model is appropriate in the subsequent analysis of deviations from plug flow reactor (e.g., Wen and Fan, 1975).

Based on the dispersion model, the pertinence of reaction rate measurements using a laminar flow reactor can be assessed. Dispersion models is an effective approach in the handling of the combined effects of radial dispersion, axial dispersion, and axial convective flow, either laminar or turbulent. The effective axial dispersion coefficient under influences of radial dispersion and axial dispersion in a laminar flow has been theoretically derived (Taylor, 1953; Aris, 1956)

$$E_z = D_M + \frac{R^2 u^2}{48 D_M} \quad (B-4)$$

Substituting the known values into the right hand side of Eq. (B-4) we obtain

$$E_z = 17.1 \text{ cm}^2/\text{s} \quad (B-5)$$

Equation (B-4) is valid when (Wissler, 1969)

$$\frac{kR^2}{(3.8)^2 D_M} < 1 \quad (B-6)$$

where k is the first order reaction rate constant; or, after substituting the system parameters,

$$k < 216. \quad (B-7)$$

For the study of NO reduction on the char surface, the feeding rate of char can be controlled to

ensure that the rate constant is below the limit in Eq. (B-7). In fact, the limit of rate constant stated in Eq. (B-7) corresponds to an extremely fast reaction and low output to input NO ratio which rarely happen in the our experimental system ($t = 0.2$ s)

$$\frac{[NO_{out}]}{[NO_{in}]} = e^{-kt} = 10^{-19} \quad (B-8)$$

From the effective axial dispersion coefficient, the Peclet number for the axial direction, Pe_z can be estimated

$$\frac{1}{Pe_z} = \frac{E_z}{uL} = 3.38 \times 10^{-2} \quad (B-9)$$

This is a very small number, implying only small deviation from the plug flow (Levenspiel and Bischoff, 1959). Levenspiel and Bischoff provided both graphic representation and equation for the correction of rate measurement

$$\frac{[NO_{out}]}{[NO_{in}]} = \exp \left[-kt + (kt)^2 \frac{E_z}{uL} \right] \quad (B-10)$$

The correction term in Eq. (B-10) indicates that the errors in measurements of rate constant will not be over 5% when the conversions is below 95%. This justifies the use our laminar flow reactor for the measurement of reaction rate.

2. Solid Mixing in Flow Reactor

When the char particle reaches the terminal velocity under free fall conditions, the weight of the particle is balanced by the sum of buoyancy force and total drag, i.e.

$$\frac{\pi}{6} d_s^3 \rho_s g - \frac{\pi}{6} d_s^3 \rho_g g + 3\pi \mu_g d_s u_s \quad (\text{B-11})$$

where d_s , ρ_s , g , ρ_g , μ_g , and u_s are char particle diameter, char nominal density, gravity, gas density, viscosity of gas, and particle velocity, respectively. Substituting the system parameters already mentioned, we obtain

$$u_s = 0.56 \text{ cm/s}$$

which is much smaller than the average gas velocity, 11 cm/s. This analysis suggests that good particles entrainment in the gas.

It is worth mentioning that char/gas mixture goes through a two-stage expansion before it reaches the reactor tube. From the reservoir, char particles are swept by a gas stream with a flow rate at 1000 cm³/min vertically into a 1/8 in tube. It expands to an 1/4 in. i.d. tube about 2 in above the reactor tube of 1.9 cm i.d. At the second expansion point, the second gas stream at 1000 cm³/min flow rate is fed horizontally at the expansion point. The two streams merge with a 90 angle, which produces rigorous mixing of solid in the gas stream.

C. Rate of NO + Char Reaction

1. Theory

In this section, the reaction rate constant is expressed in terms of NO conversion and the parameters of the flow reactor system. Carbon in the char can be gasified by NO to form CO and

CO₂. The first order NO reaction rate on char surface can be expressed as (see, e.g., De Soete, 1990)

$$r_{NO} = -kAP_{NO} \quad (C-1)$$

where: r_{NO} is the rate of NO formation, in moles (s)⁻¹ (g of char)⁻¹

A is the specific, internal surface area of char, in m²(g)⁻¹

P_{NO} is the partial pressure of NO, in atm,

k is the rate constant, in moles (s)⁻¹ (m)⁻² (atm)⁻¹.

Material balance over a small section of tubular reactor yields

$$F_{NO} + dF_{NO} = F_{NO} + (r_{NO}) dW \quad (C-2)$$

where W is the char weight and F_{NO} is the molar flow rate of NO. By the definition of conversion we obtain

$$\begin{aligned} dF_{NO} &= d(F_{NO, in}(1-X)) \\ &= -F_{NO, in} dX \\ &= -F_{NO, in} d\left(1 - \frac{C_{NO}}{C_{NO, in}}\right) \\ &= +F_{NO, in} d\left(\frac{P_{NO}}{P_{NO, in}}\right) \end{aligned} \quad (C-3)$$

where X = conversion of NO.

Substituting Eqs. (C-1) and (C-3) into Eq. (C-2) we obtain

$$F_{NO, in} d\left(\frac{P_{NO}}{P_{NO, in}}\right) = -k A P_{NO} dW \quad (C-4)$$

Rearranging the equation above we obtain

$$\frac{dP_{NO}}{P_{NO}} = \frac{-k A P_{NO, In} dW}{F_{NO, In}}$$

Integrating the equation above we obtain

$$\ln \frac{P_{NO}}{P_{NO, In}} = \frac{-k A W_t P_{NO, In}}{F_{NO, In}} \quad (C-5)$$

where W_t is the total amount of char in the reaction zone. Equation (C-5) can also be expressed in terms of conversion.

$$X = 1 - \exp\left(\frac{-k W_t A P_{NO, In}}{F_{NO, In}}\right) \quad (C-6)$$

or

$$\ln(1 - X) = \frac{-k A W_t P_{NO, In}}{F_{NO, In}} \quad (C-7)$$

Equation (C-7) can be used either for the estimation of rate constant, or the conversion if k is known.

By assuming the gas is an ideal gas mixture, the molar flow rate can be expressed as:

$$F_{NO, In} = \frac{P_{NO, In}}{P} \frac{v}{2.445 \times 10^4} \quad (C-8)$$

where the constant in Eq. (10) denotes the specific volume of gas at 25°C (in cm³/mole), and v is the total inlet volumetric flow rate measured at 25°C (in cm³/s). Substituting Eq. (C-8) into (C-7) with $P = 1$ atm and $v = 33.33$ cm³/s, we obtain:

$$\ln(1 - X) = \frac{-2.445 \times 10^4 k A W_t}{33.33} - 7.34 \times 10^2 k A W_t \quad (C-9)$$

The equation above is used in the estimation of rate constant k .

2. Experimental Results and Discussion

a. Experimental

To study the NO reduction mechanisms over a wide range of conditions, six series of experiments were conducted during this quarter, three series were with the char derived from the Pittsburgh #8 coal and three others with the char derived from Mississippi lignite. For each series, experiments were conducted over the temperature range 800 to 1100 °C with the same inlet NO concentration and a small variation in char feeding rate. NO concentrations in the feed chosen for the three series were 200, 400, and 1000 ppm. The feed gas was balanced by He. Char feeding rate varied from 0.0216 to 0.0446 g/min. These char feeding rates correspond to those used in reburning at $SR \approx 1.0$ (though no oxidant were fed in these sets of experiments) for all series, except for char derived from Pittsburgh #8 with feeding rate at 1000 ppm, $SR \approx 0.9$. Carbon monoxide and carbon dioxide were analyzed by a California Analytical Instruments' Model ZRH-2 non-dispersive infrared analyzer. Details description of the flow reactor system and experimental procedure can be found in our first and sixth quarterly reports (Chen *et al.*, 1994, 1995).

A previous collection of Pittsburgh #8 coal was used for the NO/char experiments with feed NO at 1000 ppm, and the char was prepared at 950 °C. A new Pittsburgh #8 with similar composition was used for the series with feed NO at 200 and 400 ppm. The chars for the new

Pittsburgh #8 coal and lignite were prepared at 1100 °C. This increase in char preparation temperature was due to our recent observation of reduction in surface area after NO reburning, see Section D. Since the reduction of char surface area could be contributed either by graphitization taking place at elevated temperatures (Section A; or see, e.g., Sahu *et al.*, 1988; Wong *et al.*, 1995), or by surface reaction with NO. The new procedure should eliminate the possibility of graphitization, and surface area change during reburning (or during NO/char reaction) should reveal more insights about the surface reaction mechanisms in our upcoming study.

b. Results and Discussion of Reaction Rate

The exit NO concentrations from these six series of experiments are presented in Figures 3 and 4. Exit NO concentrations decrease smoothly with increasing temperature for most of the experiments, except for the char derived from Pittsburgh #8 with NO feeding rate at 1000 ppm (Figure 4). Due to the unique feature of this curve, the experiments were repeated and the results were confirmed. This series of experiments differs from other sets of experiments from three aspects: 1) the char was prepared from our old collection of Pittsburgh #8 coal, 2) the char was prepared at 950 °C, not at 1100 °C, and, 3) the carbon to NO ratio in the feed is twice as high as those used in other five series of experiments. We plan to verify these findings with the new coal and new devolatilization temperature in the next quarter.

Reaction rates, k , at various conditions have been calculated based on experimentally observed conversion, X , and Eq. (C-9). Surface areas are determined by BET with nitrogen (N_2) as the adsorbate, see Section D. The Arrhenius plot of rate constants is presented in Figure 5. Linear regression of these data yields activation energies and preexponential factors, and they are

summarized in Table 1.

The activation energies listed in Table 1, 20 to 35 Kcal/mole, are in good accord with those in the review by De Soete (1990). The reaction rates illustrated in Figure 5 are comparably higher than those reviewed by re De Soete. At the time of this writing, we are investigating a number of potential causes of these high rates. Surface area measurement can be a potentially important source of discrepancies. As an example, the surface area of a Montana lignite char measured by BET with CO_2 was shown to be eight fold higher than the N_2 surface area (Chan, 1980). The difficulty with the BET surface area measurement has prevented Levy *et al.* (1981) from the use of internal surface area in the estimation of NO/char reaction rate constant. The rate constants reported in this report are based on N_2 surface area. Subsequent analysis of fractal dimension of internal surface area of char will eliminate this difficulty.

The other possible cause is the effects of heatup and quenching times on the conversion. The residence time was estimated based on the algorithm of Sellars *et al.* (1956). When the furnace is set at 1150 °C, the maximum wall temperature is estimated to be 50 °C lower than the maximum wall temperature and to be maintained for only 2 in of the furnace length. The residence time in this flat temperature region, 0.2 s, is considered the reaction time at 1100 °C, and residence times at other set temperatures are corrected by gas expansion or contraction using ideal gas law. The heatup and quenching times between 900 and 1100 °C also take 0.2 s, and the reaction in this section is not negligible, as shown in Figure 1 and 2.

The most interesting result observed in Figure 5 is that, in the absence of oxygen and CO_2 , the rate constants for the lignite char are consistently lower than those of the bituminous coal char. Although these rate constants remain to be corrected as discussed above, the char reactivities

presented here and the high lignite char activity during reburning observed earlier imply that the inhibition of NO reduction by oxidants, such as CO₂, may be an important step for the bituminous coal char during reburning, but may not be an important step for the lignite char. Further research about char/NO interactions in various environments in the next quarter should elucidate important information about NO reduction on lignite char in reburning.

c. Yields of Carbon Oxides and Oxygen Balance

Carbon monoxide and carbon dioxide are the principal products of NO/char reaction. Figures 6 and 7 illustrate the yields of these two components, in volume percentages, from the reaction of NO with Mississippi lignite char. The CO/CO₂ ratio is higher than one under all test conditions, but the ratio increases with increasing feed NO concentration. The oxygen recovery curves in these two figures and Figure 8 represent the total yield of carbon oxides to the reacted NO. Oxygen balances below 1050 °C are very good for five of the six series of experiments, which are consistent with the results of oxygen recovery below 900 °C reported by Chan (1980). The oxygen recoveries from the reaction of NO with lignite char at temperatures above 1050 °C is higher than 1, Figure 8, indicating gasification of oxygen in the char. The importance of char oxygen during NO reduction is not known.

D. Measurements of the Surface Fractal Dimension

A new BET apparatus (Quantachrome, NOVA-1200) has been installed in our laboratory without cost to DOE. This new apparatus reduces the operating time approximately 80% compared to that required by our original BET apparatus (Micromeritics model, Flowsorb 2300); moreover,

it does not require helium gas.

The BET-surface areas of nine samples were measured with nitrogen (N_2) as the adsorbate at a temperature of 77 K. Measurements were carried out under six different relative pressures, P/P_0 , with the multi-point method. The P/P_0 ranged from 0.05 to 0.30 was within the region of the adsorption isotherm. Each P/P_0 leads to the weight of gas, W , adsorbed on the sample. The surface area of each sample has been recovered from the Brunauer-Emmett-Teller (BET) equation,

$$\frac{1}{W(P_0/P-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_0}\right) \quad (D-1)$$

where W_m is the weight of adsorbate constituting a monolayer of surface coverage, and C is a constant. Both W_m and C are simultaneously recovered from the slope, s , and the intercept, i , of a linear plot of $1/[W(P/P_0-1)]$ against P/P_0 . This gives

$$s = \frac{C-1}{W_m C} \quad (D-2)$$

and

$$i = \frac{1}{W_m C} \quad (D-3)$$

Summing Eqs. (D-2) and (D-3) yields W_m as

$$W_m = \frac{1}{s + i} \quad (D-4)$$

Thus, the total surface area, A , is

$$A = \frac{W_m N_0 \sigma}{M} \quad (D-5)$$

where N_0 is the Avogadro number; σ , the effective cross-sectional area of an adsorbate molecule; and M , the molar weight of the adsorbate. The results are summarized in Table 2.

Additional measurements will be carried out at the same temperature, i.e., 77K, but with argon (Ar) as the adsorbate.

IV. WORK FORECAST

In the succeeding quarter, we will measure the rates of NO/chars with sequential addition of CO₂ and oxygen. Data will be compared with a Langmuir adsorption/desorption/surface reaction model. The surface area of char collected will be measured by BET method and the rates of surface reaction will be corrected by fractal dimension of char.

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Table 1. Summary of Arrhenius' constants obtained under various feed concentrations and from two different chars

	Initial NO concentration at 1000 ppm	Initial NO concentration at 400 ppm	Initial NO concentration at 200 ppm
Mississippi lignite char*	Ea = 26.2, Kcal/mole; $k_o = 6561.68$ $1/(s \cdot \text{mole} \cdot \text{m}^2 \cdot \text{atm})$	Ea = 22.3, Kcal/mole; $k_o = 16654.08$ $1/(s \cdot \text{mole} \cdot \text{m}^2 \cdot \text{atm})$	Ea = 34.2, Kcal/mole; $k_o = 2.28 \times 10^6$ $1/(s \cdot \text{mole} \cdot \text{m}^2 \cdot \text{atm})$
Pittsburgh #8 bituminous coal char†	Ea = 35.2, Kcal/mole; $k_o = 1.38 \times 10^6$ $1/(s \cdot \text{mole} \cdot \text{m}^2 \cdot \text{atm})$	Ea = 19.4, Kcal/mole; $k_o = 6178.53$ $1/(s \cdot \text{mole} \cdot \text{m}^2 \cdot \text{atm})$	Ea = 23.8, Kcal/mole; $k_o = 51862.43$ $1/(s \cdot \text{mole} \cdot \text{m}^2 \cdot \text{atm})$

* The feeding rate of Mississippi lignite char at $[\text{NO}]_{\text{in}} = 1000$ ppm is 0.0325 g/min; the feeding rate of Mississippi lignite char at $[\text{NO}]_{\text{in}} = 400$ and 200 ppm is 0.0298 g/min.

† The feeding rate of Pitt #8 bituminous coal char at $[\text{NO}]_{\text{in}} = 1000$ ppm is 0.0446 g/min; the feeding rate of Pitt #8 bituminous coal char at $[\text{NO}]_{\text{in}} = 400$ and 200 ppm is 0.0216 g/min.

Table 2. Specific surface areas measured with nitrogen as the adsorbate at a temperature of 77K.

Sample ID	Sample Name	Specific Surface Area [m ² /g]
No. 1	Mississippi lignite char	26.93
No. 2	Mississippi lignite ash/char	40.79
No. 3-1	Mississippi lignite char	70.78
No. 3-2	Mississippi lignite char/ash @SR=0.70 1100°C	36.42
No. 3-3	Mississippi lignite char/ash @SR=0.94 1100°C	51.45
No. 3-4	North Dakota lignite char	34.25
No. 3-5	North Dakota lignite char/ash 1100°C	69.00
No. 3-6	Pittsburgh #8 bituminous coal char	17.51
No. 3-7	Pittsburgh #8 bituminous coal char/ash	11.33

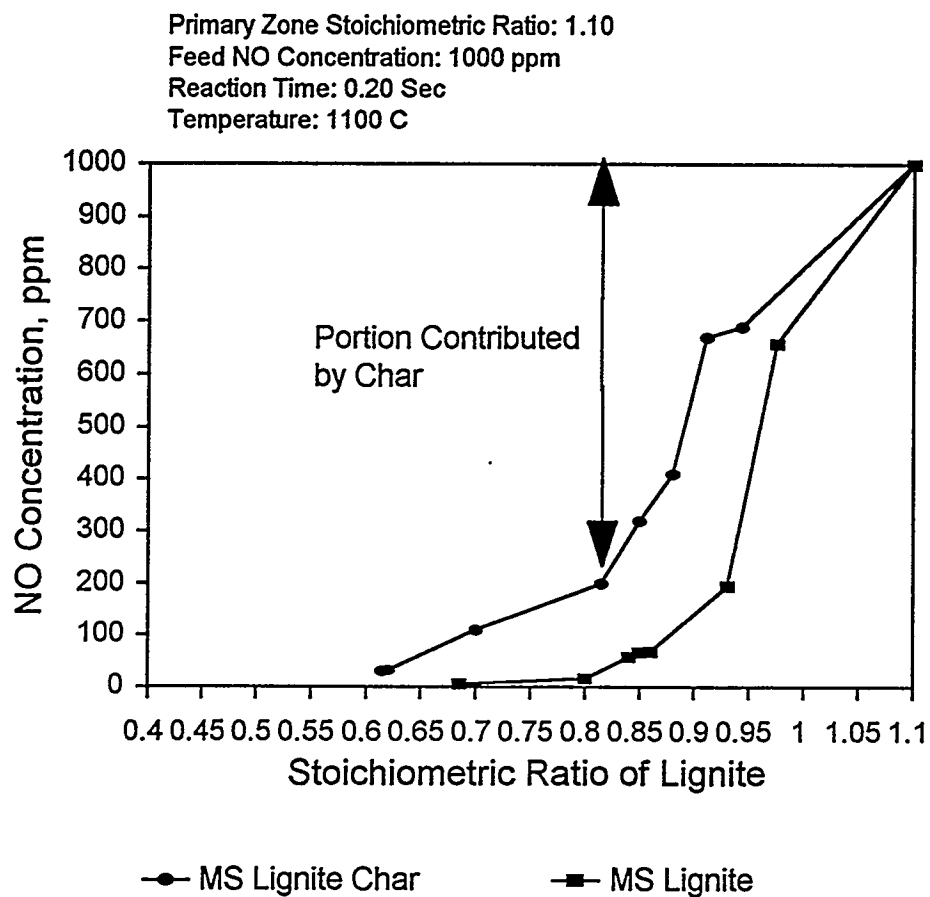


Figure 1. Heterogeneous vs. homogeneous reaction mechanisms during reburning with Mississippi lignite.

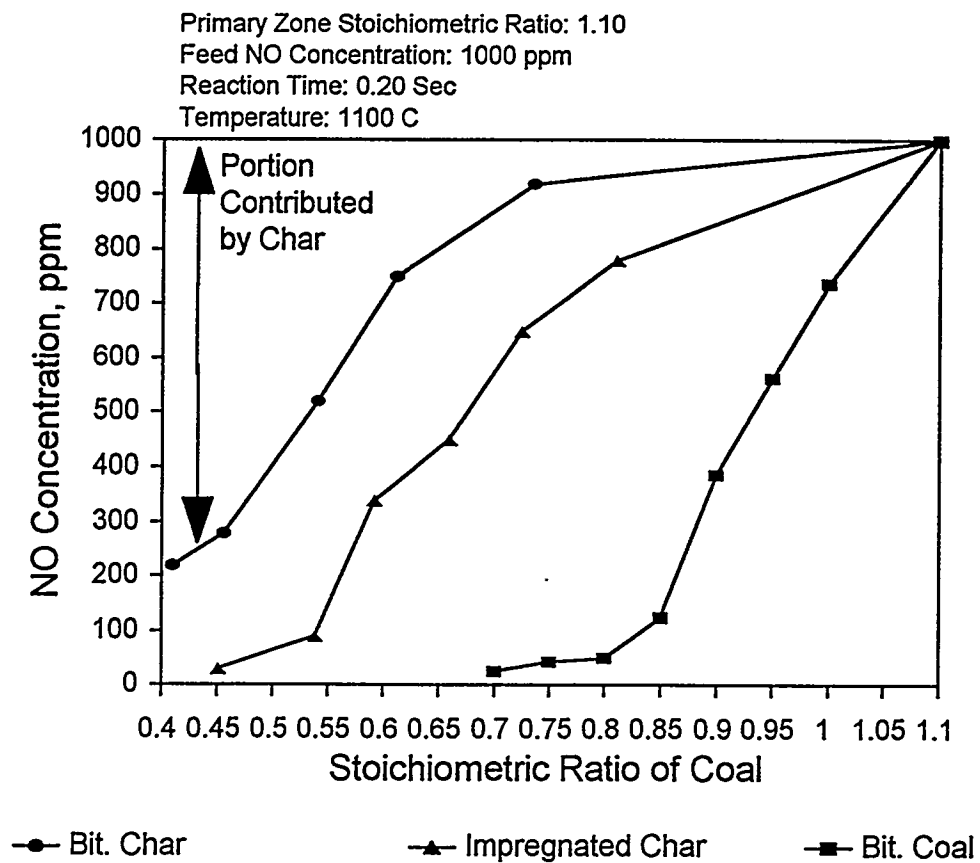


Figure 2. Heterogeneous vs. homogeneous reaction mechanisms during reburning with bituminous coal.

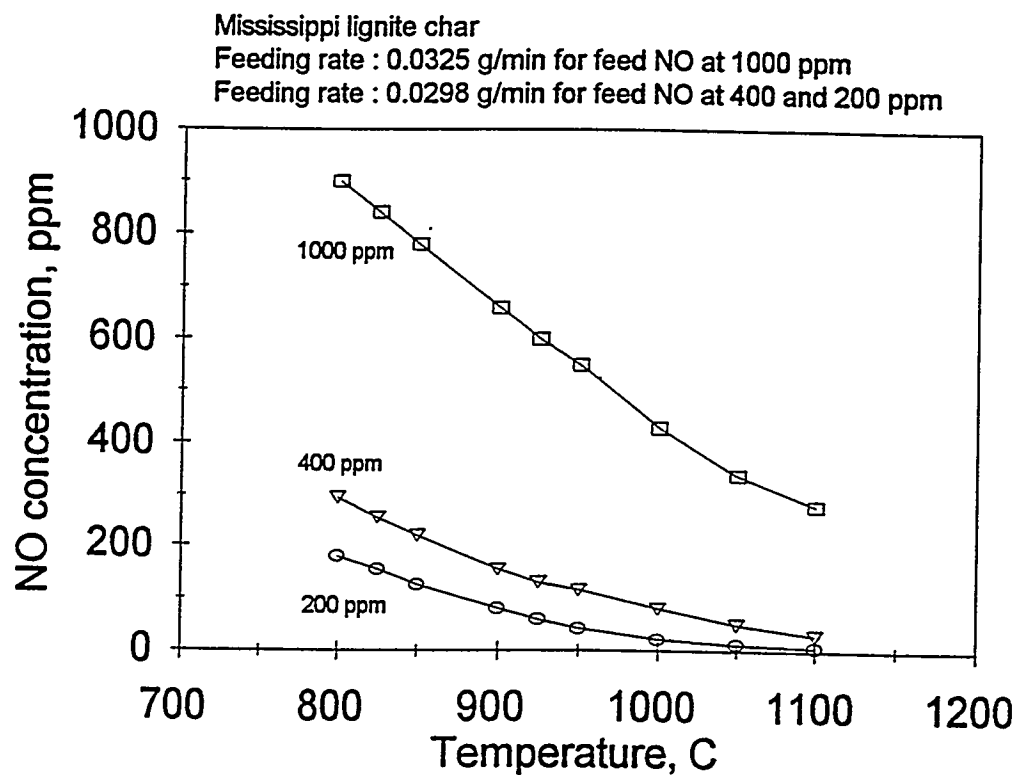


Figure 3. Exit NO concentration of NO reaction with char derived from Mississippi lignite as functions of temperature and feed NO concentration.

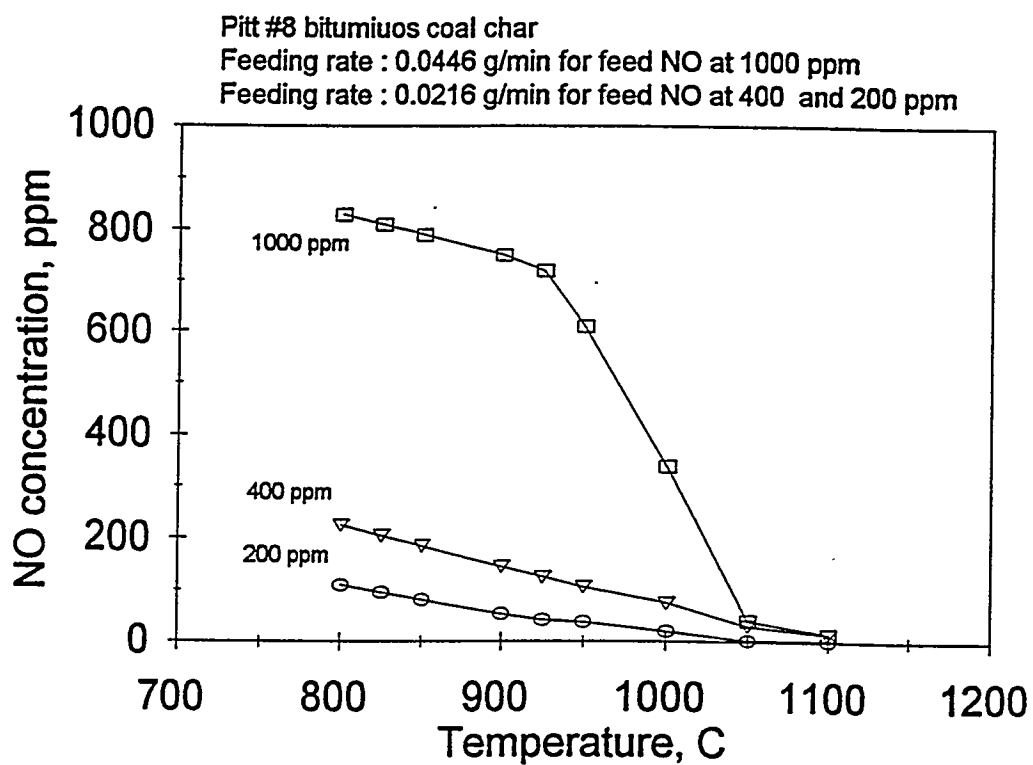


Figure 4. Exit NO concentration of NO reaction with char derived from Pittsburgh #8 coal as functions of temperature and feed NO concentration.

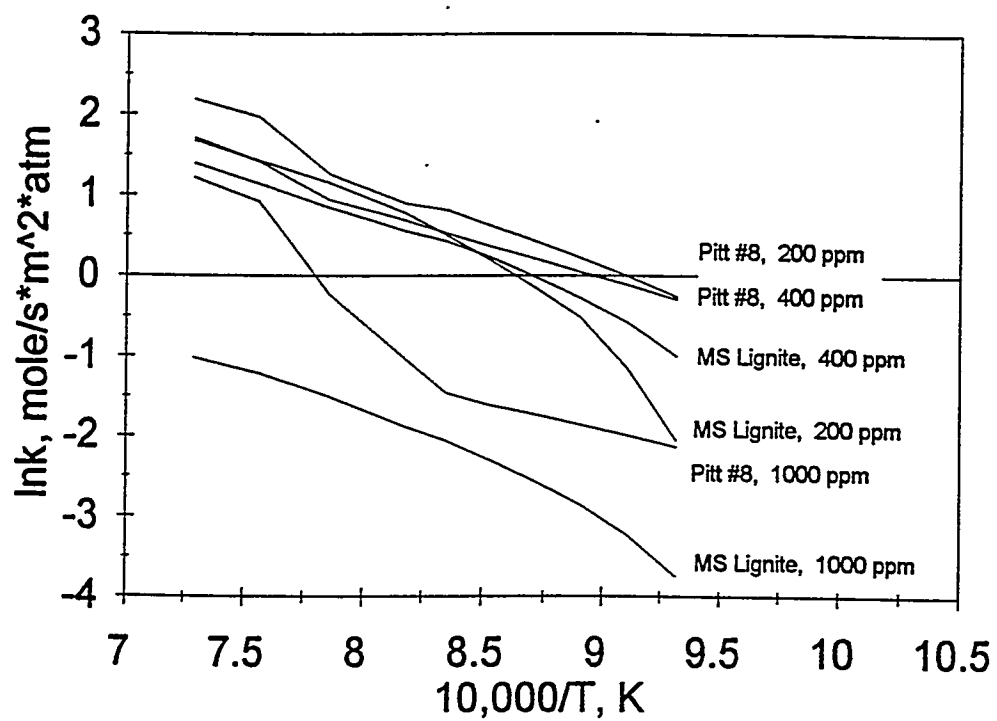


Figure 5. Arrhenius plots of NO reaction with chars of different origins and with different feed NO concentrations.

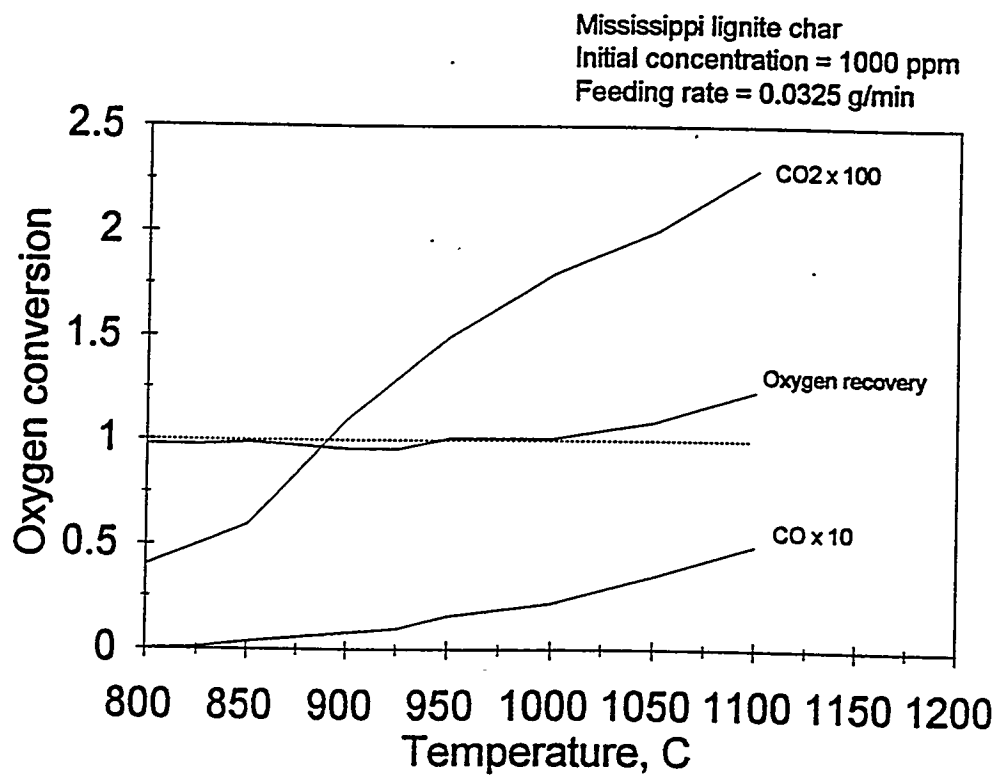


Figure 6. Yields of carbon oxides (in volume percentage) and oxygen balance (in fraction) from the reaction of NO and Mississippi lignite char with high NO to char ratio.

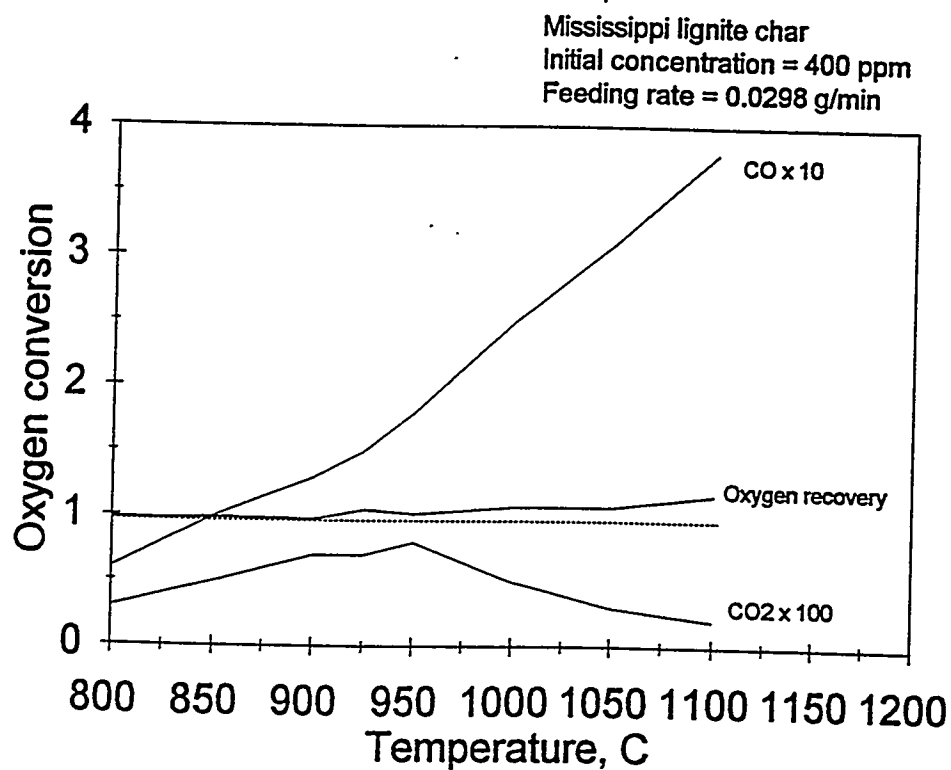


Figure 7. Yields of carbon oxides (in volume percentage) and oxygen balance (in fraction) from the reaction of NO and Mississippi lignite char with low NO to char ratio.

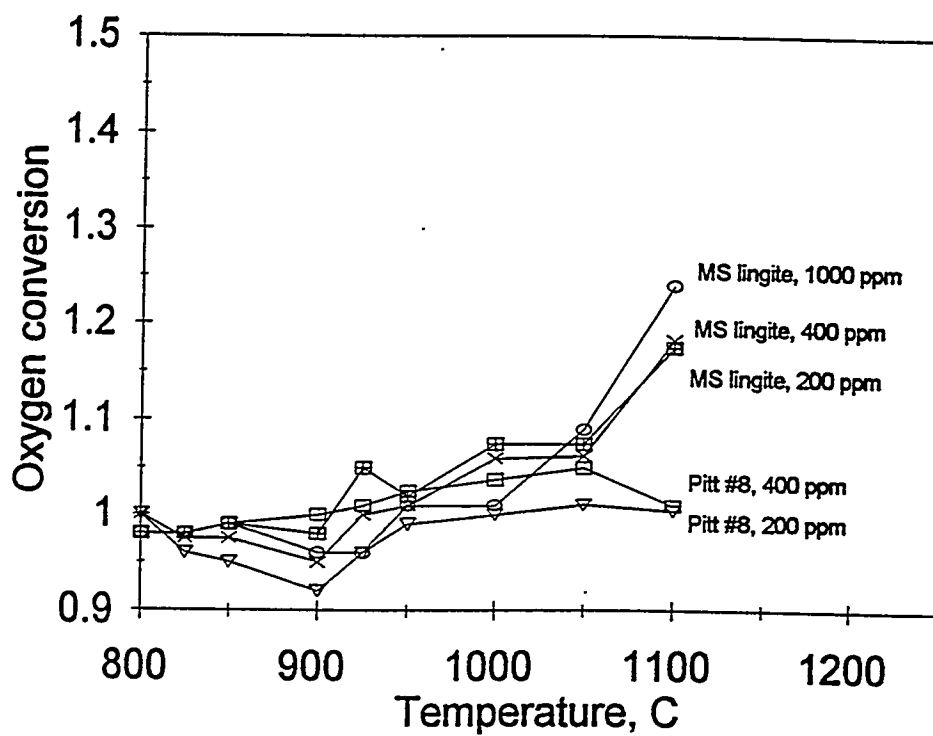


Figure 8. Oxygen recoveries of NO reaction with chars of different origins and with different feed NO concentrations.